

MICRO-XRF

Standardless and standard-supported fundamental parameter quantification of steel samples

Application Note # XRF 465

Introduction

Micro-XRF is a versatile technique for the qualitative and quantitative analysis of a vast variety of sample systems. Any standard-supported quantification requires sufficiently similar standard sets for all applications. This restriction to the flexibility of micro-XRF analysis can only be overcome by using fundamental parameter (FP) quantification algorithms. These FP methods nowadays are based on physical models for the instrumentation and on known probabilities of all physical processes involved in the X-ray fluorescence process. Therefore, they are extremely flexible with regards to different sample matrices.

Common XRF quantification is a two-step process that derives net peak intensities and then calculates the sample composition. The M4 TORNADO quantification algorithm integrates both steps. Based on an assumed sample composition, resulting XRF spectra are simulated (forward calculated) with FP. These simulated spectra are compared with the measured spectra and matched by iterating the sample properties. This approach incorpo-

rates multiple physical effects like self-absorption and secondary excitations.

Compared to the standard algorithm, the novel scheme has several advantages. Strong peak overlaps and pronounced absorption effects are treated to the best of knowledge, providing more robust results due to a larger set of fluorescence lines that can be used for the quantification.

While micro-XRF is a technique used for structured and inhomogeneous samples, bulk-FP algorithms require a homogeneous sample of infinite thickness. Thus, usually the sample itself limits the attainable quantification accuracy. For homogeneous materials, such as glasses or steels, the accuracy of FP algorithms is limited to $\pm 10\%$ by the knowledge of the physical constants.

This lab report aims to show the quality of a completely standardless FP quantification with M4 TORNADO. It also presents the possibility to even increase the result's accuracy by a one-point calibration, i.e. type calibration, making it a standard-supported FP quantification.

Sample

Technological samples, such as glasses or steels, are very homogeneous and, hence, suited to show the performance of micro-XRF analyses. Here a set of 15 certified stainless steel samples provided by the reference material supplier Analytical Reference Materials International (ARMI) were investigated. The samples needed no further preparation. The concentrations of the elements of the different steel samples are shown in Tables 1 and 2.

Measurement conditions

The measurements were performed with a Bruker M4 TORNADO. This tabletop micro-XRF spectrometer is equipped with a large vacuum sample chamber and uses a focused X-ray beam (spot size < 25 μm) to induce fluorescence in the sample. The signal is analyzed with an energy dispersive silicon drift detector (SDD). The M4 TORNADO combines high spatial resolution with fast

data processing and a high speed motorized XYZ-stage for sample positioning.

The X-ray tube settings used for the analysis were 50 kV and 200 μA . The samples were measured with a measurement live time of 60 s at a pressure of 20 mbar.

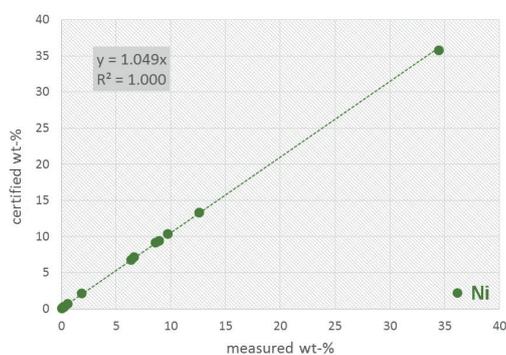
Results

Figures 1a, b show the correlation between the measured and the certified concentration values for Ni and Cr, respectively. It is evident that the results for both elements are aligned almost perfectly linear in these plots. However, the slope is not exactly 1. The incorrect slope in combination with the linearity hints to a systematic quantification error.

In the samples containing Cr, Fe, and Ni, the reason for the offset is the so-called tertiary excitation, which is a prominent effect in stainless steels: Ni fluorescence is absorbed by Fe to produce Fe fluorescence.

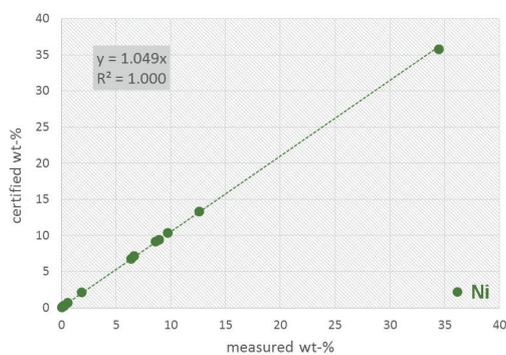
before type calibration

a)

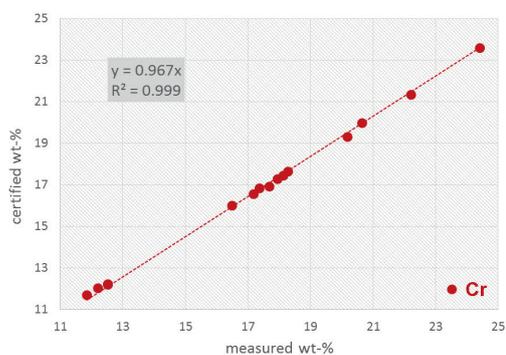


after type calibration

c)



b)



d)

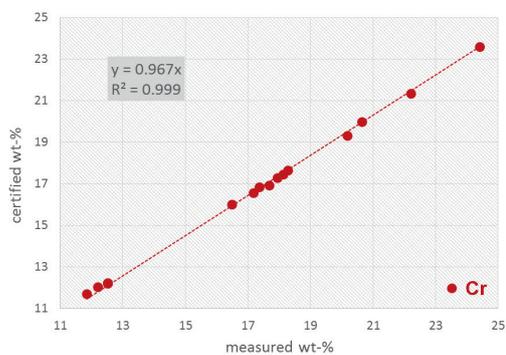


Figure 1

Correlation of the quantified values before (a, b) and after type calibration (c, d)

ARMI Reference samples			Si		Ti		V		Cr		Mn		Fe	
Grade	UNS	IARM	cert.	meas.										
Nitronic 50	S20910	17B	0.38	0.24	0.002	0.001	0.20	0.19	21.3	21.6	5.12	5.03	56.3	56.7
Nitronic 40	S21900	19B	0.48	0.39	0.006	0.000	0.10	0.08	20.0	20.1	9.31	9.44	62.3	62.5
AISI 446	S44600	14B	0.51	0.53	0.002	0.001	0.11	0.12	23.6	23.8	0.43	0.70	74.8	74.3
AISI 440C	S44004	13C	0.69	0.66	0.005	0.000	0.10	0.11	16.8	16.9	0.43	0.52	80.2	81.1
AISI 431	S43100	12B	0.56	0.58	0.003	0.001	0.04	0.04	16.0	16.0	0.60	0.74	80.1	80.3
AISI 422	S42200	205B	0.37	0.32	0.003	0.000	0.26	0.29	11.7	11.5	0.68	0.81	83.7	84.2
AISI 430	S43000	11C	0.51	0.56	trace	0.001	0.03	0.02	17.7	17.8	0.52	0.66	80.8	80.5
AISI 420	S42000	154B	0.45	0.42	0.002	0.000	0.07	0.08	12.2	12.2	0.41	0.54	86.1	86.3
AISI 416	S41600	10C	0.37	0.39	0.002	0.000	0.02	0.03	12.3	12.2	0.35	0.48	86.0	86.3
AISI 410	S41000	9C	0.35	0.28	0.002	0.000	0.08	0.09	12.0	11.8	0.38	0.51	86.2	86.6
AISI 347	S34700	8D	0.36	0.27	0.003	0.001	0.06	0.04	17.3	17.4	1.76	1.68	69.3	69.6
AISI 330	N08330	7B	1.38	1.42	0.005	0.003	0.05	0.02	19.3	19.3	1.47	1.40	41.3	41.1
AISI 321	S32100	6D	0.27	0.22	0.63	0.65	0.13	0.10	17.5	17.6	1.52	1.47	69.4	69.5
AISI 316	S31600	5D	0.46	0.40	0.008	0.007	0.03	0.01	16.6	16.7	1.78	1.71	68.2	68.4
17-7PH	S17700	152B	0.36	0.36	0.12	0.007	0.09	0.08	16.9	17.1	0.76	0.72	72.3	72.5

Table 1
Quantified compositions of reference steel samples (type calibrated) I
cert. = certified values,
meas. = measured values,

ARMI Reference samples			Ni		Cu		Nb		Mo		W	
Grade	UNS	IARM	cert.	meas.								
Nitronic 50	S20910	17B	13.4	13.4	0.17	0.17	0.22	0.20	2.30	2.31	0.093	0.100
Nitronic 40	S21900	19B	6.83	6.84	0.17	0.18	0.06	0.05	0.28	0.24	0.022	0.025
AISI 446	S44600	14B	0.29	0.24	0.07	0.06	0.006	0.001	0.10	0.07	0.011	0.009
AISI 440C	S44004	13C	0.11	0.06	0.03	0.02	0.004	0.000	0.46	0.43	trace	0.004
AISI 431	S43100	12B	2.15	2.00	0.14	0.13	0.011	0.001	0.06	0.03	0.014	0.002
AISI 422	S42200	205B	0.70	0.60	0.15	0.13	0.018	0.001	0.97	0.98	1.10	1.05
AISI 430	S43000	11C	0.22	0.16	0.07	0.06	0.005	0.010	0.06	0.04	trace	0.013
AISI 420	S42000	154B	0.22	0.17	0.09	0.07	0.003	0.000	0.08	0.06	0.010	0.000
AISI 416	S41600	10C	0.24	0.19	0.16	0.15	0.003	0.000	0.08	0.06	0.011	0.001
AISI 410	S41000	9C	0.33	0.26	0.06	0.05	0.005	0.000	0.19	0.16	0.073	0.033
AISI 347	S34700	8D	9.19	9.15	0.47	0.47	0.72	0.73	0.44	0.39	0.079	0.082
AISI 330	N08330	7B	35.8	36.0	0.21	0.25	0.023	0.012	0.19	0.16	0.031	0.056
AISI 321	S32100	6D	9.42	9.50	0.30	0.29	0.039	0.029	0.36	0.33	0.090	0.069
AISI 316	S31600	5D	10.4	10.3	0.17	0.17	0.004	0.000	2.11	2.11	0.016	0.068
17-7PH	S17700	152B	7.22	7.09	0.31	0.31	0.033	0.013	0.51	0.47	0.050	0.035

Table 2
Quantified compositions of reference steel samples (type calibrated) II
cert. = certified values,
meas. = measured values,

This Fe fluorescence in turn is absorbed by Cr in order to produce Cr fluorescence. As the MQuant routine only takes into account effects up to the second order, the tertiary excitation effect is not considered and leads to a general underestimation of the Ni content and an overestimation of the Cr content in stainless steels.

The linearity of the certified over the measured concentrations plot is valid not only for Ni and Cr but also for the other elements (see Tables 1 and 2). It allows to perform the type calibration (TC), which is a one-point calibration in the M4 TORNADO software. The type calibration is intended to correct systematic sample effects which are not accounted for in the general FP quantification. Based on the high quality of the un-biased results (without TC), the type calibration can be done using only one sample of similar composition, even though a multitude of standards is used here to illustrate the TC approach.

When plotting the certified concentration values over the measured ones (Figure 1), the slope of the resulting linear graph is the factor by which the quantification has to be scaled in order to yield a better match between measurement and certificate. The resulting correlation between the measured and the certified concentration values for Ni and Cr after performing the type calibration is shown in Figures 1c and d. The linearity did not change but the slope is much closer to 1, which means that the quantification accuracy is improved by using standards to support an FP quantification.

The type calibration can be performed for all elements of interest. Often it is sufficient to only scale the main elements. Applying the type-calibrated FP quantification to the spectra of the set of reference samples yields the results shown in tables 1 and 2 as measured values. As can be seen, there are good corre-

lations between measured and certified values not only for the major elements, such as Fe, Ni and Cr, but also for trace elements.

Similar accuracy as obtained for the reference materials after the type calibration can be expected for stainless steel samples of unknown composition. The main uncertainty remains the sample itself with its inhomogeneity on the micrometer scale.

It has to be noted that for the fluorescence lines of minor and trace elements, an overlap with diffraction peaks may lead to an overestimation of the elemental content (please refer to Lab Report XRF 463 and 464). Those diffraction peaks usually can be averted by using primary beam filters for the measurement.

Conclusion

The fundamental parameter quantification of the M4 TORNADO yields good results for a wide variety of samples. If for specific sample types systematic effects impede the desired quantification accuracy, a type calibration for this sample type can be performed by use of a single sample of known composition or more, if available.

In this example, the tertiary excitation effect in steels was corrected for based on a set of reference samples. The correction factors are easily derived by plotting the certified compositions against the measured ones. Applying these correction factors to the calibration reduces the deviation from the certified values to < 0.5 % for a large range of element concentrations.

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